

Monitoring of Kr and Xe Isotopes in Air Using Liquid Oxygen

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Abstract—A method was developed for determining radioactive Kr and Xe isotopes in air using liquid technical-grade oxygen prepared at air-separation plants. Kr and Xe are less volatile air components than N₂ and O₂ and are therefore accumulated in liquid oxygen in the course of its production. The method allows determination of background volumetric concentrations of Kr and Xe at short distances (~100 km) from the sources of radioactive noble gas (RNG) injection. The results of ⁸⁵Kr and ^{133,135}Xe monitoring in air of St. Petersburg in 2006–2008 are presented. For some air samples taken in St. Petersburg, back trajectories of the transfer of air masses were calculated, using HYSPLIT dispersion transport model developed by ARL, to determine possible sources of injection of Xe and ⁸⁵Kr radionuclides.

Keywords: *radioactive noble gas monitoring, volumetric concentrations of krypton and xenon isotopes in air, liquid technical-grade oxygen, transfer of air masses*

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An efficient method for monitoring safe operation of plants of nuclear power engineering is monitoring of gas–aerosol discharges in zones of location of such objects. In so doing, data on the concentrations of Xe and Kr in air are very valuable and bear important information. Direct isolation of Kr and Xe from air is very difficult, because their weight fraction in air is low: 1.14×10^{-4} and 0.87×10^{-5} vol %, respectively. Therefore, to determine background concentrations of Kr and Xe radionuclides, it is, as a rule, necessary to process large (no less than 5 m³) air samples. These problems can be overcome by using those products from air-separation plants in which Kr and Xe are concentrated. A Kr–Xe mixture produced as by-product in oxygen production at metallurgical plants or liquid oxygen produced on smaller but more widespread air-separation plants can be used for this purpose. For monitoring of Kr and Xe radionuclides in St. Petersburg in 2006–2008, we used liquid technical-grade oxygen produced at an air-separation plant in the northern part of St. Petersburg near the Khlopin Radium Institute site.

EXPERIMENTAL

The process for preparing from liquid oxygen Kr and Xe samples suitable for spectrometric analysis consisted of liquid oxygen sampling, its gasification,

RNG adsorption on an inorganic sorbent, subsequent desorption, and transfer of Kr and Xe into a measuring ampule.

Liquid oxygen samples were taken into a 5-l Dewar vessel from the liquid oxygen pouring system. Then the sample was delivered to a laboratory and processed into a spectrometric sample. The procedure was as follows: first step, gasification of liquid oxygen and sorption of Kr and Xe on an inorganic sorbent; second step, desorption of Kr and Xe from the inorganic sorbent and their transfer into a spectrometric ampule.

Liquid oxygen gasification was performed in a specially fabricated gasifier. It was a ~1-l cylindrical metallic vessel with two welded-in gas-outlet pipes and a hole with a threaded stopper for filling with liquid oxygen. For gasification, liquid oxygen was poured into the vessel from which it spontaneously evaporated without special heating. With the progress of evaporation, oxygen was intermittently added into the gasifier until the oxygen from the Dewar vessel was fully exhausted.

After the last addition of the liquid oxygen, the pouring hole was tightly stoppered and the flow of the vaporizing oxygen was directed to a sorber packed with NaX zeolite. To enhance the sorption efficiency, the sorber was placed in a foamed plastic thermostat.

To the lower part of the thermostat, we added liquid nitrogen in such an amount that the lower part of the sorber (~1.5–2.0 cm) was in liquid nitrogen. The gasifier and sorber were connected to each other with a vacuum hose. The connection lines were equipped with pressure–vacuum gauges and with a bypass line for emergency relieve of excess pressure. The excess pressure in the system in the course of gasification was maintained at 0.1–0.15 MPa by controlling the gas flow rate at the sorber outlet. After the gasification completion, the sorber was taken off from the thermostat and allowed to warm up to room temperature. The gas discharge from the sorber was continued until stable excess pressure not exceeding 0.1 MPa was attained.

Then the gas mixture in the sorber was desorbed, and Kr and Xe were trapped in a glass ampule packed with SKT-3 activated carbon. For this purpose, the sorber was placed in a furnace heated to 150°C. Helium was fed to the sorber inlet through a reductor at a flow rate of 50–60 cm³ min⁻¹. A radon trap and a measuring ampule were connected to the sorber outlet with a vacuum hose. The ampule was placed in a cooling mixture with a temperature of 163–173 K (mixture of ethanol with liquid nitrogen). In the course of heating the sorber, the gases from the zeolite were desorbed and passed through a measuring ampule with a helium flow. In the ampule, Kr and Xe underwent low-temperature sorption. The content of Kr and Xe in the gas flow was monitored with a gas chromatograph. After the Xe release from the sorber ceased, the desorption was stopped. The measuring ampule was taken off from the cooling mixture and allowed to warm up to room temperature. In the process, the excess pressure over 0.1 MPa was discharged to the atmosphere. After that, measurements were performed with a γ -ray spectrometer equipped with a well Ge detector. The γ -ray spectra of the Xe and Kr isotopes were recorded simultaneously. The exposure time for single measurement was 20–24 h.

After the completion of γ -spectrometric measurements, the content of Kr and Xe in the measurement ampule was determined. To this end, the ampule was placed in a furnace heated to 150°C, and helium was passed through it at a rate of ~10 cm³ min⁻¹. As receiver we used a 50 cm³ glass syringe. After mixing of the gases in the syringe, the volumetric concentration of Kr and Xe in the gas mixture was determined with a gas chromatograph. From the volumetric concentration of Kr and Xe in the syringe, we calculated their content in the ampule.

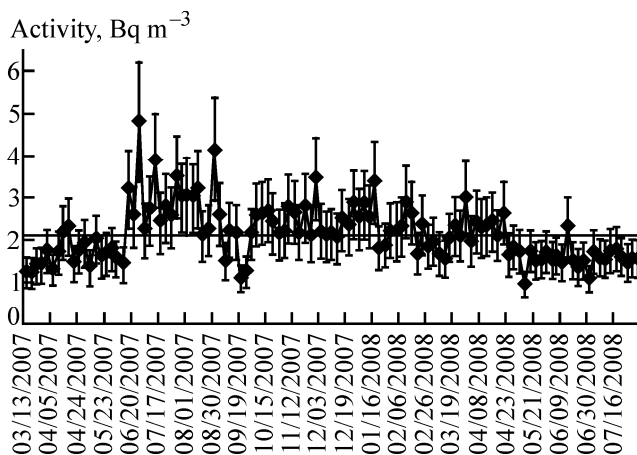


Fig. 1. ⁸⁵Kr activity in air of St. Petersburg in the period 2007–2008; the line denotes the mean value (2.11 ± 0.66 Bq m⁻³).

RESULTS AND DISCUSSION

Following the above-described procedure, we performed monitoring of Xe and ⁸⁵Kr radioisotopes in St. Petersburg air in 2007–2008. Liquid oxygen samples were taken twice a week. The results of determining the ⁸⁵Kr volume activity in St. Petersburg air in this period are shown in Fig. 1.

As can be seen, the ⁸⁵Kr activity in air varied in a wide range, from 0.92 to 4.80 Bq m⁻³, with a mean value of 2.11 Bq m⁻³. The median is close to the mean value: 2.09 Bq m⁻³. In some cases, low ⁸⁵Kr concentrations were detected, such as 0.92, 1.08, and 1.07 Bq m⁻³. This very interesting result is probably associated with the transfer of air masses from the north or with the measurement uncertainty. As seen from Fig. 1, fluctuations of the ⁸⁵Kr activity in St. Petersburg air exceed the uncertainty of a single measurement. Therefore, it will be interesting to find the source of the ⁸⁵Kr discharge, which can be done using data on the transfer of air masses. It should be noted that there is no correlation between the ⁸⁵Kr and ¹³³Xe concentrations, i.e., the release (discharge) of long- and short-lived radionuclides is separated in time. As far as we now, the gas treatment system at nuclear power plants consists of several lines, e.g., of two or three lines. Noble gases are sorbed on one line and kept for the decay of the short-lived radionuclides on the other lines. This is followed by the sorbent regeneration, and the remaining ⁸⁵Kr ($T_{1/2} = 10.2$ years) is desorbed from the system and, most probably, discharged to the atmosphere. The short sampling time in St. Petersburg allowed us to reveal air

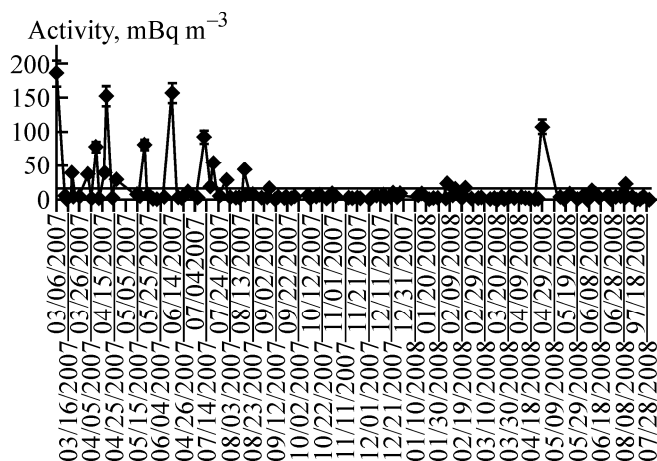


Fig. 2. ^{133}Xe activity in air of St. Petersburg in the period from January 2007 to July 2008; the line denotes the mean ^{133}Xe activity (11.7 mBq m^{-3} ; median 1.9 mBq m^{-3}).

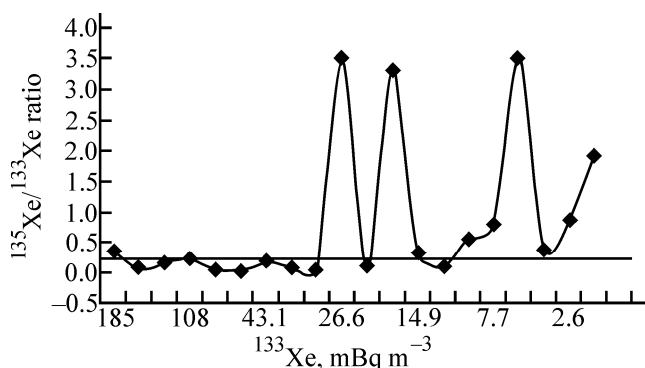


Fig. 3. Variation of the $^{135}\text{Xe}/^{133}\text{Xe}$ activity ratio in St. Petersburg air samples; the line denotes the median.

samples enriched in ^{85}Kr relative to the mean values.

The ^{85}Kr monitoring in Japan [1], Ireland [2], and Germany [3] also revealed periods of its increased ($5\text{--}8 \text{ Bq m}^{-3}$) concentration, which is due to discharges from spent fuel reprocessing plants.

Monitoring of Xe Radionuclides in St. Petersburg

The results of the ^{133}Xe monitoring in air in St. Petersburg in the period from January 2007 to July 2008 are shown in Fig. 2. As can be seen, during the monitoring period the ^{133}Xe activity varied from the background level ($<0.2 \text{ mBq m}^{-3}$) to 185 mBq m^{-3} . The mean ^{133}Xe activity in this period was 11.7 mBq m^{-3} ($n = 126$), with high rms deviation, 30 mBq m^{-3} , suggesting large fluctuations of the activity. The median for this observation period was

1.9 mBq m^{-3} . In the same period, we obtained several samples (16%) containing also ^{135}Xe ($T_{1/2} = 9.14 \text{ h}$). The $^{135}\text{Xe}/^{133}\text{Xe}$ activity ratio varied from 0.033 to 3.5. No correlation was found between the concentrations of the Xe radionuclides; it is only clear that ^{135}Xe was present only in samples in which the ^{133}Xe activity exceeded 30 mBq m^{-3} , but not in all such samples. For example, on March 29 and on April 2 and 9, 2007, the ^{133}Xe activity exceeded 30 mBq m^{-3} , but ^{135}Xe was not detected in these samples. Analysis of the back trajectories shows that, in the days when ^{135}Xe was detected in air samples, the air masses were transferred from the west. This matter will be discussed in more detail below.

In Fig. 3, the $^{135}\text{Xe}/^{133}\text{Xe}$ activity ratio in air samples is plotted vs. ^{133}Xe activity. According to [4, 5], the $^{135}\text{Xe}/^{133}\text{Xe}$ activity ratio at equilibrium in the reactor zone reaches 0.24–0.33. Comparison of the experimental ratios with the equilibrium values allows, using radionuclide chronometry, calculation of the time between the release of Xe isotopes from the reactor and the measurement of the air sample taken.

As seen from Fig. 3, in approximately a half of the samples, the $^{135}\text{Xe}/^{133}\text{Xe}$ activity ratio is lower than the equilibrium value, i.e., presumably, the transfer of air masses in this case took much time.

Determination of Possible Sources of Xe and ^{85}Kr Radionuclide Release

For each case of air sampling in St. Petersburg, we calculated the back trajectories of air mass transfer using the HYSPLIT dispersion transport model developed by ARL (<http://www.arl.noaa.gov/ready.html>).

Considering the results of monitoring of Kr and Xe radionuclides in St. Petersburg, let us pay attention to cases of recording high concentrations with two Xe radionuclides present in the sample. These data are collected in the table. They show that the air mass transfer in these periods occurred from the sector from south to north–northwest, with no transfer from eastern directions.

The calculated trajectories for St. Petersburg, September 5, 2007 (Fig. 4), show that the air masses arrived from the regions of Forsmark NPP (Sweden, 60.40°N , 18.25°E) and Olkiluoto NPP (Finland, 61.5°N , 21.5°E).

Figure 5 shows the scheme of transfer trajectories for the period from 11:00, January 15 to 11:00, Janu-

Volume activity of ^{133}Xe and ^{135}Xe in air of St. Petersburg in the period from September 2007 to July 2008 and directions of air mass transfer

Sampling date ^a	Volume activity as for sampling date, mBq m^{-3}		$^{135}\text{Xe}/^{133}\text{Xe}$ activity ratio	Particle transfer direction	Suggested source
	^{133}Xe	^{135}Xe			
09/05/2007	14.9 ± 0.6	5.0 ± 0.5	0.34	NNW, W	Forsmark (Sweden), Olkiluoto (Finland)
01/14/2008	7.7 ± 1.2	6.1 ± 0.9	0.79	W	Forsmark, Leningrad NPP
01/16/2008	6.4 ± 0.5	22.7 ± 1.0	3.5	SW, S	Ignalina NPP
02/16/2008	26.6 ± 2.7	93 ± 10	3.5	SW	Ignalina NPP
02/21/2008	19.2 ± 2.0	63 ± 6.0	3.3	W	Leningrad NPP
04/10/2008	1.9 ± 0.2	3.7 ± 0.3	1.9	SW, S	Barsebäck, Oskarshamn
04/28/2008	108 ± 11	25.0 ± 3.0	0.23	SW, W	Leningrad NPP
07/09/2008	24 ± 2	2.5 ± 0.4	0.10	NNS	Kola NPP

^a 10–11 h MSK.

ary 16 (GMT). The trajectory passed over Ignalina (Lithuania) on January 15 at approximately 19:00 GMT at a height of approximately 400 m. The air mass that arrived at St. Petersburg was enriched in ^{135}Xe , with the $^{135}\text{Xe}/^{133}\text{Xe}$ ratio equal to 3.5. The transfer took about 12 h; therefore, by the moment of RNG release in the region of Ignalina NPP this ratio should be almost two times higher.

On February 6, 2008, the air masses transferred to St. Petersburg in the period from 11:00 to 17:00 (GMT) were enriched in ^{135}Xe , with the $^{135}\text{Xe}/^{133}\text{Xe}$ ratio increased from 3.5 to 9.8. Figure 6 shows the

two-day back trajectories for the sampling date of February 6, 2008. Analysis of the back trajectories (Fig. 6) suggests that the air masses were directly over Ignalina at a height of approximately 300 m, i.e., throughout the 6-h period the air masses were transferred to St. Petersburg from the Ignalina region at a relatively small height. The time of transfer of the air mass from Ignalina to St. Petersburg is about 18 h.

On April 28, 2008, the ^{133}Xe concentration in St. Petersburg increased considerably, to 108 mBq m^{-3} , with the $^{135}\text{Xe}/^{133}\text{Xe}$ ratio equal to 0.23. Analysis of the back trajectories (Fig. 7) shows that, during a period of

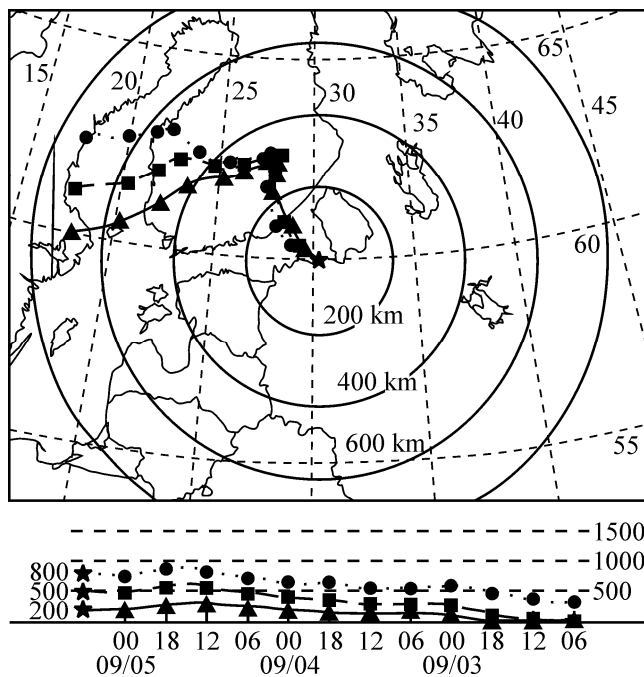


Fig. 4. Three-day back trajectories to St. Petersburg, 06:00 GMT, September 5, 2007.

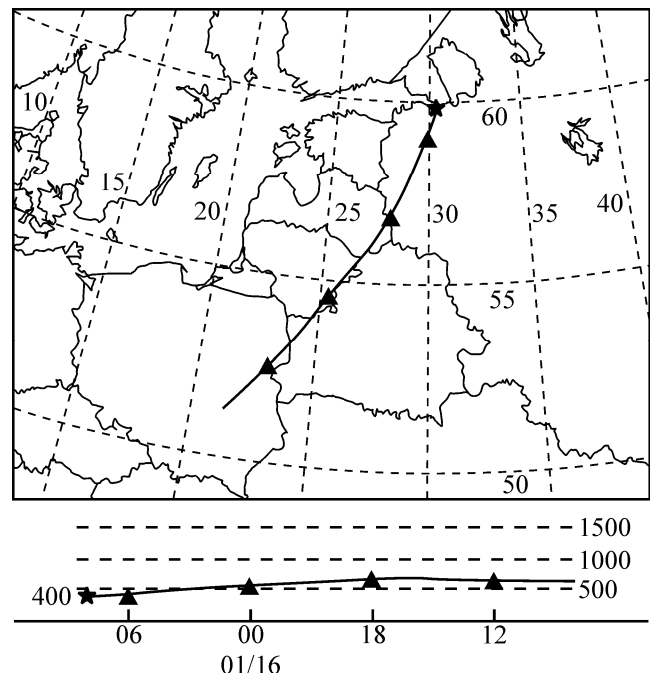


Fig. 5. One-day back trajectory at a height of 400 m to St. Petersburg, 08:00 GMT, January 16, 2008.

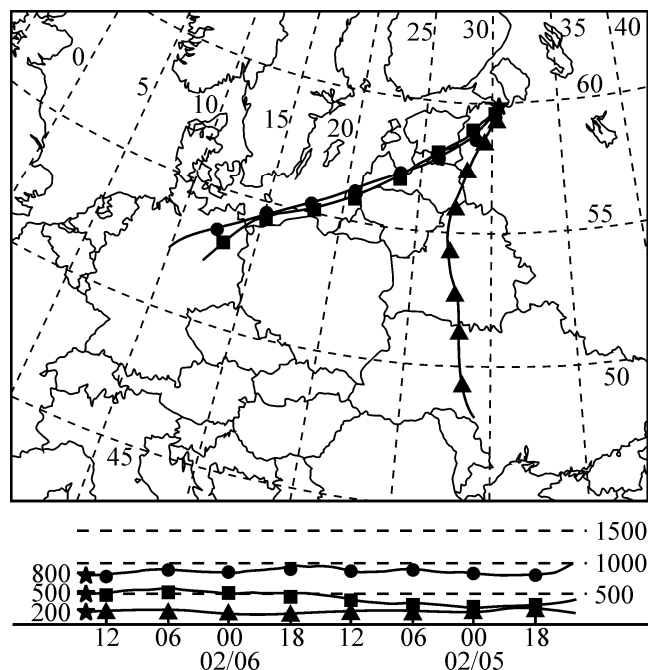


Fig. 6. Two-day back trajectories to St. Petersburg, 14:00 GMT, February 6, 2008.

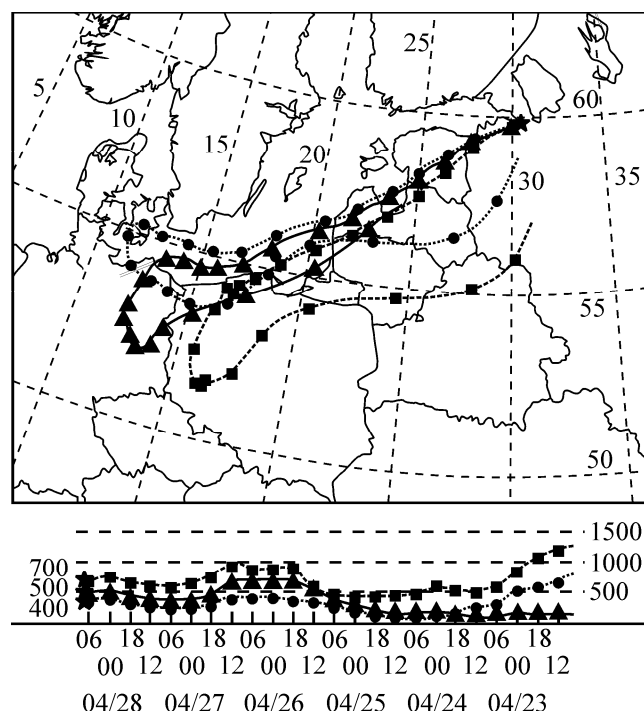


Fig. 7. 144-h back trajectories at heights of 400, 500, and 700 m to St. Petersburg, 07:00 GMT, April 28, 2008

5 days, the air mass at a height of 400 m passed in the immediate vicinity of the southern coast of Sweden, near Barsebäck NPP. The Xe radionuclides could originate from the Barsebäck NPP in southern Sweden

or from Leningrad NPP in Sosnovyi Bor. If these masses had arrived from southern Sweden, then nine half-lives of ^{135}Xe would elapse in 84 h, and by the moment of release the $^{135}\text{Xe}/^{133}\text{Xe}$ would be about 70, which considerably exceeds the calculated value for NPPs and for plants producing radiopharmaceuticals (e.g., Fleurus, Belgium). Therefore, most probably, air masses with such a high content of Xe radionuclides and indicated ratio were transferred from the region of Leningrad NPP.

As seen from the table, on July 9, 2008 the $^{135}\text{Xe}/^{133}\text{Xe}$ activity ratio was ~ 0.1 , and the ^{133}Xe activity was almost 80 times higher than the background level. The three-day back trajectories at all the heights were similar, starting from the southern end of Novaya Zemlya and passing over the Barents Sea, Kola Peninsula, Finland, and Karelia to St. Petersburg. At approximately 0 h on July 7, the air mass trajectory passed in the immediate vicinity of Polyarnye Zori town (Kola NPP). More than five ^{133}Xe half-lives passed during the 2-day period of the flow of the air masses, and hence by the moment of the gas release the ratio of these radionuclides should be about 2.8. There are good grounds to believe that RNGs were transported from the region of Polyarnye Zori town (Kola NPP).

On December 13 and 24, 2007, on January 21, 28, and 30, and on February 18, 20, and 26, 2008, the ^{133}Xe concentration in the air of St. Petersburg was either minimal or on the level of the procedure sensitivity and did not exceed $0.2\text{--}0.5\text{ mBq m}^{-3}$. Analysis of the back trajectories for the period of 1–3 days prior to sampling showed that, on December 13, the air masses in the 200–1000 m layer flew to St. Petersburg from the central regions of the Barents Sea and from northern regions of the Scandinavian Peninsula. On December 24, there was stable transfer from west–southwest, with the trajectory passing 15 km to the south from the Leningrad NPP. On January 21, 2008, the transfer was from the south-eastern region of Sweden, and on January 28 the 1-day trajectory passed over northern regions of Finland and Karelia, arriving at St. Petersburg from the north; the trajectories originate over the North Sea and pass at a height of 200 m through Sweden, Gulf of Bothnia, southern end of Finland, and eastern part of the Gulf of Finland. On January 30, at heights of 500 and 800 m, the trajectories pass more northerly, through central regions of Scandinavia and Finland. On February 18, there was stable transfer from the northwest, originating in northern Finland (levels 500

and 800 m) and northern Sweden (level 200 m). Thus, analysis of the meteorological pattern shows that the minimal (background) concentrations of ^{133}Xe in St. Petersburg were observed, as a rule, when the air mass trajectories passed at large distances from NPPs or passed over NPPs in periods when the RNG release from them was minimal.

Analysis of the calculated back trajectories of the air mass transfer shows that, in most cases, short periods of increased ^{85}Kr concentration in air of St. Petersburg can be associated with the transfer of air masses from the regions of NPP location. In four cases, the air masses mainly arrived from the region of Ignalina NPP, and in two cases, from Kalinin and Kola NPP. Because ^{85}Kr is neither utilized nor disposed of, the accumulated ^{85}Kr is intermittently discharged into the atmosphere. Considerable increase in the ^{85}Kr concentration (by a factor of 10–20) was observed in previous years in 1-day samples in Ireland [2] and in 1-week samples in Japan [1].

Thus, 2-year monitoring of the concentration of radioactive noble gases in the Southwestern Region of Russia allowed us to determine the limits of variation of the Xe and ^{85}Kr radionuclide concentrations in St. Petersburg and to reveal possible sources of the release of these radionuclides on the basis of meteorological data. We found that the minimal ^{133}Xe activity in air of St. Petersburg did not exceed 0.2 mBq m^{-3} , with the maximal value reaching 185 mBq m^{-3} . The mean ^{133}Xe activity in the observation period was 11.7 mBq m^{-3} . In the same period, in 21 samples we detected ^{135}Xe ; its maximal concentration was 93 mBq m^{-3} .

In St. Petersburg located at a distance of 80 km from the Leningrad NPP, the ^{133}Xe activity level is considerably higher than in Cherepovets, where we also performed monitoring of Kr and Xe radionuclides [6]. In contrast to Cherepovets, in St. Petersburg in some cases we detected two Xe radionuclides: ^{133}Xe and ^{135}Xe , with their ratio varying in a wide range, suggesting the effect of other objects apart from Leningrad NPP. In transfer of air masses from the west, St. Petersburg is under the effect of Swedish and Fin-

nish NPPs. Although the concentration of radioactive noble gases in air is not subject to regulations and is considerably lower than the Rn concentration, it seems necessary to continue such monitoring. Its results will confirm for the public the safety of the modern nuclear power engineering, especially taking into account its further development in the nearest future.

Our studies showed that the release of Xe and ^{85}Kr radionuclides can be detected at long distances from the emission source. The presence of two radionuclides, ^{133}Xe and ^{135}Xe , in air samples allows estimation of the distance from the emission source to the sampling point. Using the available atmospheric transfer models, it is possible to calculate the radionuclide concentrations at the moment of emission. Measurement of Kr and Xe isolated from liquid oxygen samples furnishes information on the radionuclide content for a relatively narrow time interval.

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